

A state-of-the-art review of biomass torrefaction, densification and applications



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ABSTRACT

Torrefaction is a mild pyrolysis, which has been explored for the pretreatment of biomass to increase the heating value and hydrophobicity. Due to its potential applications for making torrefied pellets, which can be used as a high quality feedstock in gasification for high quality syngas production and as a substitute for coal in thermal power plants and metallurgical processes, torrefaction and densification have attracted great interest in recent years from both academia and bioenergy industry. This paper provides a comprehensive review of research progresses in this area, drawing on major contributions from two major research groups of the authors on torrefaction and densification at Canada and Taiwan as well as literatures. It is revealed that torrefaction of various biomass species and their major components, lignin, cellulose and hemicelluloses have been extensively studied in thermogravimetric apparatus (TGA) under both inert (N₂) and oxidative (O₂, H₂O) environments to elucidate the weight loss as a function of temperature, particle size and time. It was found that the higher heating value and saturated water uptake of torrefied biomass were a strong function of weight loss, which represents the degree of torrefaction. When torrefied sawdust is compressed into torrefied pellets, more mechanical energy is consumed and higher die temperature is required to make torrefied pellets of similar density and hardness as regular pellets. Simple economics analyses based on laboratory scale experimental data showed that because of the potential savings from pellets transport, handling and storage logistics, the overall cost for torrefied pellets can be lower than regular pellets in European market for both European and Canadian pellets. The gasification could be improved in terms of both energy efficiency and syngas quality because of the removal of oxygenated volatile compounds from torrefied biomass.

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1. Introduction

With increasing global population and rising living standards, there has been a significant growth in energy demand worldwide over the last several decades. This leads to diminishing fossil fuel reserves, serious environmental pollution and high greenhouse gas (GHG) emissions. To address these challenges, many efforts in developing renewable energy and alternative fuels have been carried out and substantial progress has been made. Although the applications of renewable energy grow rapidly lately, their applications are still limited due to the high cost, poor technology reliability, and limited resource availability. Among the renewable energy and alternative fuels under development, biomass energy or bioenergy is one of the promising resources to match the requirements of substituted fossil fuels for reducing GHG emissions.

Biomass can be considered as one of the solar energy resources. Plants grow by absorbing carbon dioxide from the atmosphere as well as water and nutrients from soils followed by converting them into hydrocarbons through photosynthesis. All carbon contained in biomass is gained from carbon dioxide; in other words, carbon is cycled in the atmosphere when biomass is consumed as a fuel. Therefore, biomass is referred to as a carbon neutral fuel when it is burned [1]. On account of the wide distribution of biomass on the Earth's surface, bioenergy has a great potential as a low-carbon source for large-scale energy production. In fact, bioenergy is the largest renewable energy source so far, which accounts for around 10% of primary energy demand in the world, according to the International Energy Agency (IEA) [2].

Biomass can be transformed into gas or liquid fuels via a variety of methods, such as gasification, pyrolysis, anaerobic digestion, fermentation and transesterification. It can also be utilized as a solid fuel and burned directly for the generation of heat and power. However, biomass is characterized by its high moisture content, low calorific value, hygroscopic nature and large volume or low bulk density, which result in a low conversion efficiency as well as difficulties in its collection, grinding, storage and transportation. For those reasons, biomass is usually blended with coal for co-firing rather than used alone in power plants [3]. In the past, a number of biomass pretreatment methods have been developed to address the aforementioned disadvantages. Among the explored biomass upgrading methods, torrefaction and densification (or pelletization) are two noticeable routes for solid fuel production. A search for the number of journal papers in Scopus (Sciencedirect.com) made on November 4, 2014, using the keyword of “torrefaction” and restricted to Abstract, Title, Keywords, showed more than 449 papers published in this subject, as displayed in

Fig. 1a. Similarly, using the keywords of “biomass” and “pelletization” reveals a growing interest in this area, as shown in Fig. 1b. The profiles in Fig. 1 suggest that the research and development of torrefaction and densification for bioenergy applications are very active worldwide.

Torrefaction and densification have demonstrated numerous merits in improving the properties of biomass, and possess a great potential for industrial applications. Torrefaction was recently reviewed by van der Stelt et al. [4] and Chew and Doshi [5], with a focus on the torrefaction without covering densification of torrefied biomass to torrefied pellets. This review is intended to provide a comprehensive overview of recent development in the torrefaction and densification process with a focus on the fundamental characteristics of biomass torrefaction for the production of torrefied pellets and the properties of torrefied pellets. Their potential industrial applications and economics will be discussed as well.

2. Lignocellulosic structure and properties of biomass

The constituents in biomass include cellulose (a polymer glucosan), hemicelluloses (which are also called polyose), lignin (a complex phenolic polymer), organic extractives and inorganic minerals (also called ash). The first three constituents are the main components in biomass and their weight percents depend on biomass species. For example, the softwood typically consists of 42% cellulose, 27% hemicelluloses, 28% lignin and 3% organic extractives; the hardwood comprises 45% cellulose, 30% hemicelluloses, 20% lignin and 5% organic extractives [6]. Inorganic minerals are usually less than 1% of the content in wood. A clear understanding of the nature and behavior of these constituents is conducive to elucidating biomass torrefaction and densification characteristics.

Cellulose is a linear homopolysaccharide composed of β -D-glucopyranose units linked together by (1 $\rightarrow$ 4)-glycosidic bonds [7]. Crystalline and amorphous structures are contained in cellulose and can be expressed by $(C_6H_{10}O_5)_m$ where subscript m is the degree of polymerization. Hemicellulose is a branched mixture of various polymerized monosaccharides, such as xylose, glucose, mannose, galactose, arabinose and glucuronic acid [8]. Its basic structure can be represented by $(C_5H_8O_4)_m$. Lignin is a three-dimensional, highly branched and polyphenolic substance that consists of an irregular array of variously bonded “hydroxy-” and “methoxy-” substituted phenylpropane units [9]. Its chemical formula is represented by $[C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7}]_m$ [10]. Based on the chemical formulas of the three constituents, the atomic O/C

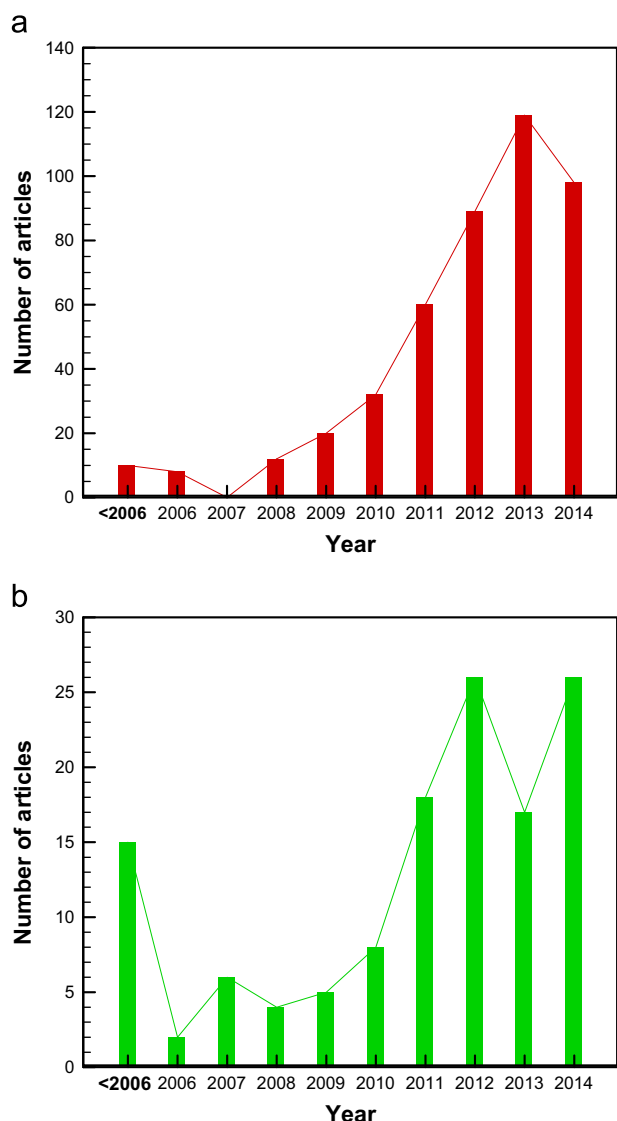


Fig. 1. Number of papers concerning (a) torrefaction and (b) pelletization published in the last decade (by November 4, 2014).

ratios in cellulose, hemicellulose and lignin are found to be 0.83, 0.80 and 0.47–0.36, respectively, and their atomic H/C ratios are 1.67, 1.6 and 1.19–1.53, respectively. In view of their distinct compositions and structures, cellulose, hemicellulose and lignin possess different thermal decomposition characteristics. Generally speaking, the thermal decomposition temperature (TDT) of hemicellulose is the lowest among the three constituents at the range of 220 and 315 °C. Cellulose decomposes at temperatures between 315 and 400 °C. Lignin is featured by gradual decomposition for the temperature ranging from 160 to 900 °C [11]. Figs. 2a and b show the typical thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of the standard samples of cellulose (Alfa Aesar, A17730), hemicellulose (SIGMA, X-4252), lignin (Tokyo Chemical Industrial Co., L0045), xylose (SIGMA, X-1500) and glucose (Panreac Quimica SA, 131341). In some biomass samples, the decomposition peaks of cellulose and hemicellulose from DTG can be identified clearly [12], whereas the two peaks overlap in some biomass samples so that it is hard to be distinguished. The properties of cellulose, hemicellulose and lignin are summarized in Table 1.

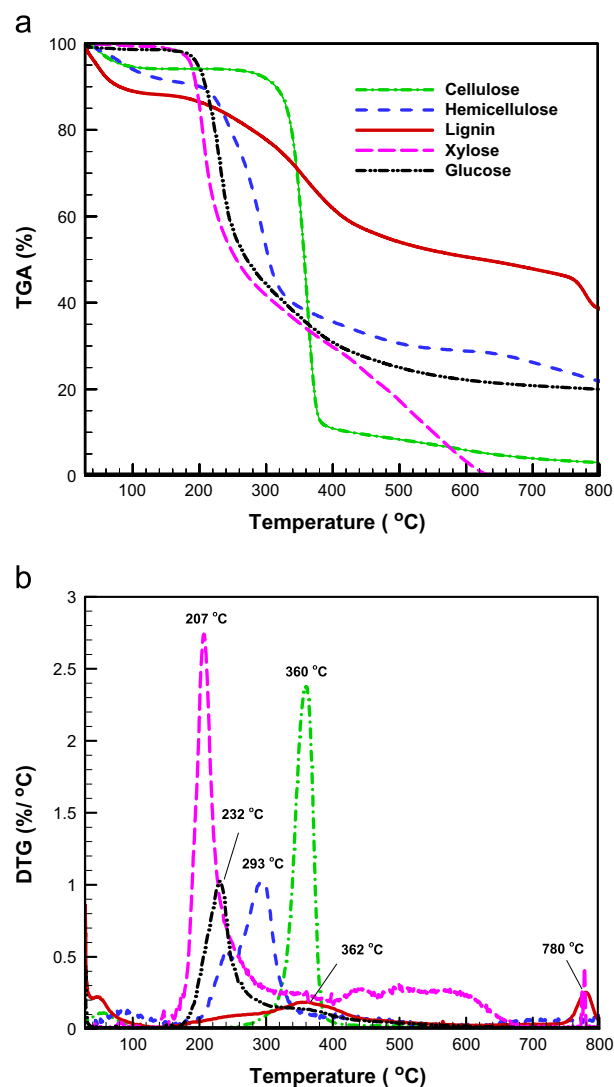


Fig. 2. (a) Thermogravimetric analyses (TGA) and (b) derivative thermogravimetric (DTG) analyses of the standards of cellulose, hemicellulose, and lignin. (No reference).

3. Torrefaction

3.1. Torrefaction process

Torrefaction pertains to a thermal pretreatment of biomass where raw biomass is heated in an inert atmosphere at temperatures of 200–300 °C for the purpose of upgrading solid biomass fuel [13]. Nitrogen is the commonly used carrier gas to provide a non-oxidizing atmosphere in most laboratory tests. Since torrefaction is conducted at conditions similar to those of pyrolysis which usually takes place between 350 and 650 °C [14], torrefaction has also been called mild pyrolysis. As described earlier, raw biomass is characterized by its high moisture content, low calorific value, hygroscopic nature, and larger volume or low bulk density. The evidences from recent research suggest that after undergoing torrefaction the properties of biomass are improved to a great extent [4,5]. The benefits accomplished by torrefaction include (1) higher heating value or energy density; (2) lower atomic O/C and H/C ratios and moisture content; (3) higher hydrophobicity or water-resistivity; (4) improved grindability and reactivity; and (5) more uniform properties of biomass. Fig. 3 shows a summary of changes in biomass properties before and after torrefaction.

Table 1
Summary of the properties of cellulose, hemicellulose, and lignin in biomass.

	Cellulose	Hemicellulose	Lignin
Structure	Linear	Branched	Three-dimensional
Formula	$(C_6H_{10}O_5)_m^a$	$(C_5H_8O_4)_m$	$[C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7}]_m$
Atomic O/C	0.83	0.80	0.47–0.36
Atomic H/C	1.67	1.60	1.19–1.53
TDT ^b (°C)	315–400	220–315	160–900
Component	Glucose	Xylose, glucose, mannose, galactose, arabinose and glucuronic acid	Phenylpropane
Thermal behavior	Endothermic (exothermic if char formation is significant)	Exothermic	Exothermic

^a *m*: degree of polymerization.

^b TDT: thermal decomposition temperature.

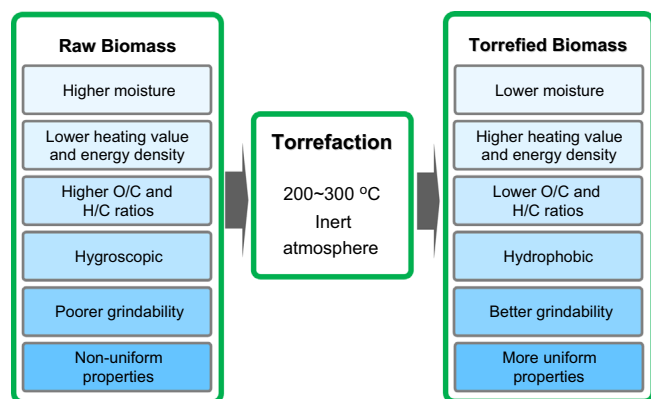


Fig. 3. A schematic of property variation of biomass undergoing torrefaction.

When biomass is torrefied, the pretreatment can be further classified into light, mild and severe torrefaction processes, corresponding to the temperatures of approximately 200–235, 235–275 and 275–300 °C, respectively [9]. With light torrefaction, the moisture and low molecular weight volatiles contained in biomass will be released. Hemicellulose in biomass is the most active constituent among hemicellulose, cellulose and lignin; it is thermally degraded to a certain extent from light torrefaction, whereas cellulose and lignin are only slightly or hardly affected [15]. Therefore, the weight loss of biomass is slight and its energy density or calorific value increases only slightly. When biomass undergoes mild torrefaction, hemicellulose decomposition and volatile liberation are intensified. Hemicellulose is substantially depleted and cellulose is also consumed to a certain extent. With regard to severe torrefaction, hemicellulose is almost depleted completely and cellulose is oxidized to a great extent. Lignin is the most difficult constituent to be thermally degraded; its consumption within the temperature range of torrefaction is thus very low. Hemicellulose and cellulose are the main constituents of biomass. By virtue of substantial removal of hemicellulose and cellulose from biomass by severe torrefaction, the weight and energy yield of biomass are usually lowered significantly although the energy density of the fuel is intensified to a great extent. A comparison among light, mild and severe torrefaction is given in Table 2.

In addition to temperature, torrefaction time or duration is another important factor in determining the performance of torrefaction. Torrefaction can be carried out between several minutes [16,17] to several hours [18]. The energy density of produced solid fuel is enhanced from torrefaction, and an increase in duration raises the carbon content and energy intensity. For example, in the study of Felfri [19], when wood briquettes were torrefied at 250 °C for 0.5, 1 and 1.5 h, the higher heating values of the biomass increased from 20.0 to 21.2, 22.1 and 22.7 kJ kg^{−1}, respectively. However, more energy for the

Table 2
Torrefaction classification and torrefaction products.

Classification	Light	Mild	Severe
Temperature (°C)	200–235	235–275	275–300
Consumption			
Hemicellulose	Mild	Mild to severe	Severe
Cellulose	Slight	Slight to mild	Mild to severe
Lignin	Slight	Slight	Slight
Liquid color	Brown	Brown dark	Black
Product			
Gas	H ₂ , CO, CO ₂ , CH ₄ , toluene, benzene and C _x H _y		
Liquid	H ₂ O, acetic acids, alcohols, aldehydes and ketones		
Solid	Char and ash		

thermal pretreatment is required if torrefaction duration is extended. From the TGA of biomass [12], the thermal degradation of biomass is rapid at torrefaction time less than 1 h, and becomes very slow beyond 1 h. Therefore, torrefaction is normally controlled within 1 h [6,5,12]. Overall, within the typical operating ranges of temperature and residence time, the influence of reaction temperature on the properties of biomass prevails over the residence time. Different combinations of temperature and residence time can be used to achieve a given degree of torrefaction, as represented by the weight loss [6]. On the other hand, the key properties of the torrefied product, such as higher heating value and saturated moisture uptake, are primarily determined by the weight loss [20–22].

3.2. Torrefaction behavior and products

The thermal behavior of biomass torrefaction plays a crucial role in controlling the pretreatment process and determining torrefaction performance. Specifically, the temperature control in the reactor will be disturbed by the endothermic and exothermic reactions in the course of torrefaction, thereby influencing the quality of solid products. As described earlier, cellulose, hemicellulose and lignin are the main constituents in biomass. Therefore, the thermal behavior of biomass in torrefaction is highly related to the endothermic and exothermic reactions of the preceding constituents. Basically, the pyrolyses of hemicellulose and lignin are exothermic in nature [23] and a higher content of lignin in biomass led to the higher exothermicity in a biomass decomposition process [24]. In contrast, the pyrolysis of cellulose is endothermic. However, cellulose pyrolysis could be driven in the exothermic direction by the charring process which competed with tar formation [25], thereby reducing the heat required for biomass pyrolysis. In other words, the char yield is the main factor to change the thermal behavior of cellulose pyrolysis. Past studies [25–27] have suggested that cellulose pyrolysis at higher pressures as well as lower carrier gas flow rate, heating rate, and temperature has a trend to intensify the charring process. The

Table 3

A list of fixed carbon (FC), volatile matters (VM), atomic O/C and H/C ratios as well as higher heating values of various types of biomass before and after torrefaction.

Biomass	<i>T</i> (°C)	<i>t</i> (min)	FC ^a (wt%)	VM ^a (wt%)	O/C ^b	H/C ^b	HHV (MJ kg ^{−1})	Reference
Bagasse								Chen et al. [43]
Raw			14.6	80.7	0.713	1.211	18.3	
Torrefied	250	60	25.9	66.8	0.486	1.124	20.9	
	300	60	42.2	45.9	0.207	0.789	23.4	
Bamboo								Rousset et al. [15]
Raw			17.8	80.1	0.747	1.636	18.2	
Torrefied	220	60	22.5	75.2	0.668	1.442	19.3	
	250	60	29.2	67.9	0.570	1.255	21.0	
	280	60	37.8	58.8	0.464	1.047	23.1	
Banyan								Chen et al. [10]
Raw					0.755	1.579	18.5	
Torrefied	230	60			0.519	1.533	22.9	
	260	60			0.352	1.276	25.8	
	290	60			0.256	1.127	28.0	
Beech								Ohliger et al. [29]
Raw			16.1	83.3	0.649	1.532		
Torrefied	270	40	22.7	76.3	0.474	1.340		
	290	40	32.4	66.7	0.382	1.131		
	300	40	41.9	56.6	0.316	1.030		
Eucalyptus								Arias et al. [61]
Raw			9.4	89.8	0.683	1.494	19.4	
Torrefied	240	30	22.3	77.0	0.573	1.379	22.2	
	240	60	23.4	75.6	0.579	1.336	21.8	
	240	180	23.9	75.1	0.558	1.338	21.9	
	280	30	30.6	68.3	0.458	1.142	23.4	
	280	60	35.5	62.8	0.365	1.002	25.0	
	280	180	37.0	61.4	0.409	1.103	25.9	
Leucaena								Wannapeera et al. [18]
Raw			13.1	86.1	0.626	1.772	20.3	
Torrefied	200	30	14.0	85.3	0.588	1.648	21.0	
	250	30	16.9	82.2	0.565	1.449	21.2	
	250	120	22.1	76.6	0.555	1.249	21.2	
	275	30	24.9	73.8	0.479	1.154	22.8	
Microalgae								Wu et al. [40]
Raw			21.0	70.1	0.397	2.000	20.5	
Torrefied	200	30	20.7	70.2	0.375	1.675	21.9	
	250	30	27.2	61.5	0.239	1.452	21.8	
	300	30	36.5	49.7	0.122	1.298	25.9	
Oil palm fiber								Lu et al. [11]
Raw			20.5	72.5	0.651	1.205	17.1	
Torrefied	250	60	27.3	63.8	0.480	1.017	20.1	
	275	60	32.4	56.6	0.445	0.945	21.4	
	300	60	44.3	41.2	0.300	0.739	23.4	
Pine								Phanphanich and Mani [39]
Raw			13.8	86.0	0.727	1.688	18.5	
Torrefied	225	30	15.0	84.8	0.668	1.472	19.5	
	275	30	23.3	76.4	0.521	1.355	21.8	
	300	30	40.9	58.7	0.353	1.052	25.4	
Reed canary grass								Bridgeman et al. [61]
Raw			12.1	82.4	0.576	1.679	19.5	
Torrefied	250	30	13.3	80.3	0.552	1.503	20.0	
	270	30	16.1	76.6	0.536	1.379	20.8	
	290	30	21.3	70.4	0.501	1.348	21.8	
Rice husk								Chen et al. [43]
Raw			10.1	79.5	0.727	1.197	17.5	
Torrefied	250	60	22.9	63.6	0.522	1.156	17.7	
	300	60	42.2	34.1	0.238	0.712	21.5	
Sawdust								Chen et al. [65]
Raw			15.0	84.5	0.717	1.812	18.8	
Torrefied	230	20	19.6	71.8	0.622	1.358	20.3	
	250	30	24.3	66.3	0.565	1.275	20.7	
	290	30	36.5	50.7	0.398	1.013	22.4	
Spruce								Broström et al. [66]
Raw			14.6	85.2	0.644	1.479	20.3	
Torrefied	260	8	15.7	84.0	0.617	1.377	20.6	
	260	25	19.3	80.3	0.560	1.321	21.5	
	285	16.5	22.3	77.3	0.526	1.217	22.2	
Willow								Bridgeman et al. [62]
Raw			10.7	87.6	0.600	1.563	20.0	
Torrefied	230	30	16.1	82.1	0.584	1.467	20.2	
	270	30	18.6	79.3	0.522	1.371	21.4	
	290	30	20.5	77.2	0.499	1.316	21.9	

Table 3 (continued)

Biomass	T (°C)	t (min)	FC ^a (wt%)	VM ^a (wt%)	O/C ^b	H/C ^b	HHV (MJ kg ⁻¹)	Reference
Wheat straw								Bridgeman et al. [62]
Raw			17.3	76.4	0.598	1.725	18.9	
Torrefied	250	30	15.6	77.0	0.538	1.476	19.8	
	270	30	26.5	65.1	0.480	1.364	20.7	
	290	30	38.0	51.8	0.367	1.191	22.6	
SPF shaving								Peng et al. [21]
Raw			6.8	93.0	0.665	1.494	18.1	
Torrefied	240	60	15.3	84.5	0.591	1.382	20.9	
	270	60	26.0	73.7	0.461	1.172	23.1	
	300	60	35.8	63.8	0.361	1.017	25.3	
	340	60	50.6	48.9	0.236	0.796	29.5	

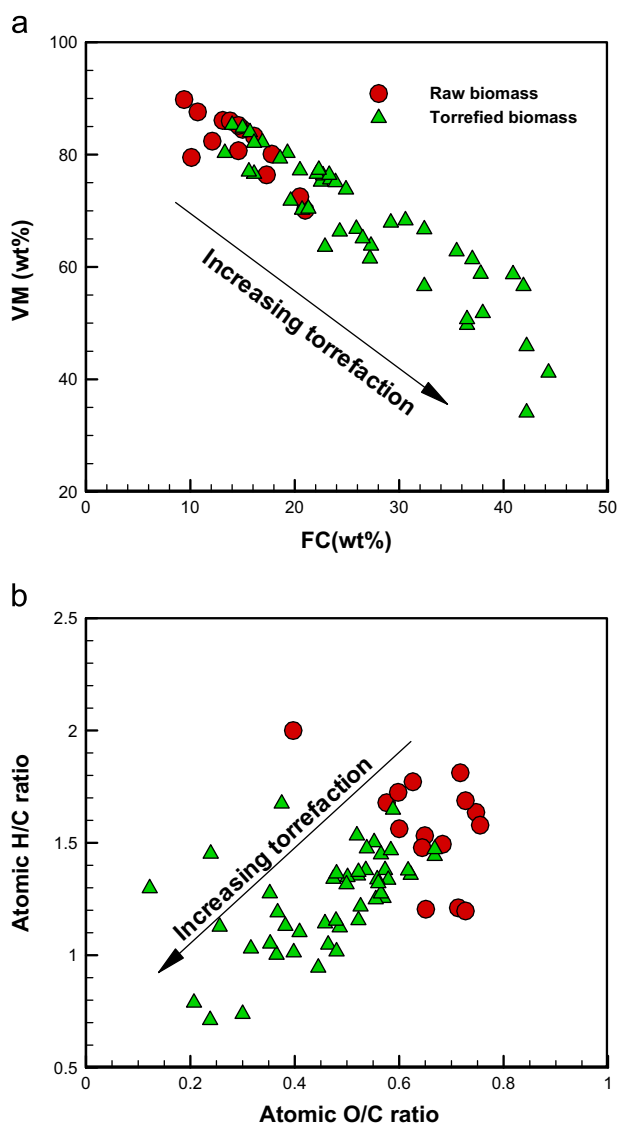
^a Dry basis.^b Dry basis and atomic ratio.

Fig. 4. The plots of (a) fixed carbon versus volatile matter and (a) van Krevelen diagram of biomass species.

pyrolysis even became exothermic at low temperatures because of the dominant mechanism of char formation [22]. The endothermic and exothermic characteristics of cellulose, hemicellulose, and lignin are also summarized in Table 1.

Recently, a few studies concerning the thermal behavior of biomass torrefaction have been carried out. Bates and Ghoniem

[28] developed a model using a two-step and first-order mechanism to describe willow torrefaction. They found that the exothermic behavior at the first torrefaction stage was between -40 and -280 kJ kg⁻¹, while the thermal behavior of the second stage depended on temperature. Ohliger et al. [29] studied the torrefaction of beechwood chips to evaluate the heat of reaction in a lab-scale reactor. They reported that the heat of reaction was between -199 and 148 kJ kg⁻¹ at torrefaction temperatures of 270 – 300 °C and residence time of 15 – 60 min. van der Stelt [30] performed beechwood torrefaction in a fixed bed reactor for 30 min to measure the heat of reaction. Corresponding to the torrefaction temperatures of 230 , 250 and 280 °C, the values of heat of reaction for beechwood torrefaction were in the ranges of 425 – 1113 , 22 – 1375 , and -1516 – 1160 kJ kg⁻¹, respectively. These data indicate that the beechwood torrefaction process was less endothermic or more exothermic with increasing torrefaction temperature.

The solid fuel is the primary product from torrefaction, although the gas and liquid products are also obtained [31]. The non-condensable gas product comprises primarily CO, CO₂, H₂ and small amount of CH₄ [32]; toluene, benzene and low molecular weight hydrocarbons are also detected. The gas product typically contains 10% of the energy of biomass. Because of the low heating value of the gas product, its application is limited. The liquid product is brown or black colored, depending on the torrefaction temperature [9], and consists of condensable components, such as water, acetic acids, alcohols, aldehydes and ketones [33]. The analysis of liquid product from gas chromatography–mass spectrometry (GC–MS) suggests that the main components in the liquid are monoaromatics; small amounts of heterocyclic hydrocarbons are also obtained at a torrefaction temperature as high as 280 °C [9]. A brief summary of gas, liquid and solid products from torrefaction are given in Table 2, and the properties of torrefied biomass will be discussed in detail below.

3.3. Properties of torrefied biomass

3.3.1. Moisture content

Moisture content is an important property of biomass fuels, because a high moisture level in a fuel leads to a high energy loss in the course of burning. As a feedstock, it is desirable to lower the moisture content of biomass. For example, the biomass feedstock must be dried to a moisture content below 30 wt% in the synthesis gas production process, preferably to about 15 wt%, and to below 10 wt% in the pyrolysis process [34]. To increase the energy efficiency, improve the energy product quality and reduce the emissions in the thermochemical energy conversion process, the reduction of biomass moisture content plays a vital role [35]. In addition, biomass with less moisture can be stored stably over extended period of time, with a low risk of biological deterioration. Also, the transportation of hydrophobic solids is less expensive, as a consequence of less moisture to be delivered along with the biomass.

Table 4

A list of solid yield, higher heating values, energy yield, and energy ratio of various types of biomass before and after torrefaction.

Biomass	<i>T</i> (°C)	<i>t</i> (min)	SY ^a (%)	HHV ^b (MJ kg ^{−1})	EF ^c (–)	EY ^d (%)	Reference
Wood briquettes							Felfri et al. [19]
Raw				20.02	1		
Torrefied	220	60	90.00	20.99	1.048	94.36	
	250	60	65.00	22.06	1.102	71.62	
	270	60	54.00	22.98	1.148	61.98	
Wheat straw							Bridgeman et al. [61]
Raw				18.90	1		
Torrefied	250	30	82.60	19.82	1.049	86.20	
	270	30	71.50	20.70	1.095	78.20	
	290	30	55.10	22.60	1.196	65.80	
Rape stalk							Deng et al. [44]
Raw				18.75	1		
Torrefied	200	30	63.29	19.50	1.040	65.82	
	250	30	38.26	20.10	1.072	41.01	
	300	30	25.30	21.59	1.151	29.13	
Loblolly pine							Yan et al. [38]
Raw				19.52	1		
Torrefied	250	80	83.80	20.92	1.070	89.70	
	275	80	74.20	21.77	1.120	83.10	
	300	80	60.50	23.52	1.210	73.20	
Rice husk							Pimchuai et al. [63]
Raw				14.32	1		
Torrefied	250	60	77.50	15.89	1.110	86.00	
	270	60	74.25	16.07	1.120	83.33	
	300	60	58.25	17.59	1.230	71.56	
Wood							Chen et al. [10]
Raw				20.70	1		
Torrefied	220	60	82.98	23.23	1.122	93.12	
	250	60	54.73	27.52	1.329	72.76	
	280	60	47.22	28.38	1.371	64.74	
Leucaena							Wannapeera et al. [18]
Raw				20.30	1		
Torrefied	225	30	86.50	21.20	1.040	90.33	
	250	30	73.00	21.20	1.040	76.24	
	275	30	54.50	22.80	1.120	61.21	
Logging residue chips							Phanphanich and Mani [39]
Raw				18.79	1		
Torrefied	250	30	81.00	21.21	1.129	92.00	
	275	30	70.00	22.03	1.172	82.00	
	300	30	52.00	26.41	1.406	72.00	
Bamboo							Chen et al. [59]
Raw				18.70	1		
Torrefied	230	60	49.36	24.31	1.300	64.17	
	260	60	40.92	26.11	1.396	57.13	
	290	60	37.98	26.14	1.398	53.09	
Empty fruit bunches							Uemura et al. [45]
Raw				17.02	1		
Torrefied	220	30	43.16	17.17	1.009	43.54	
	250	30	36.98	17.67	1.038	38.39	
	300	30	24.18	20.41	1.199	29.00	
Coffee residue							Chen et al. [47]
Raw				20.37	1		
Torrefied	240	30	89.41	21.78	1.069	95.60	
	240	60	84.01	22.87	1.123	94.30	
	270	30	74.13	25.34	1.244	92.20	
	270	60	64.12	28.06	1.378	88.33	
Norway spruce							Broströma et al. [65]
Raw				20.30			
Torrefied	260	25	89.20	21.50	1.059	94.50	
	285	16.5	80.30	22.20	1.094	87.90	
	310	25	45.90	27.80	1.369	62.80	
Eucalyptus							Lu et al. [11]
Raw				18.40	1		
Torrefied	250	60	83.60	20.60	1.120	93.70	
	275	60	75.80	21.50	1.168	88.50	
	300	60	57.90	23.90	1.299	75.40	
Pitch pine							Park et al. [46]
Raw				18.42			
Torrefied	250	30	86.60	20.46	1.111	96.20	
	275	30	81.40	22.21	1.206	98.20	
	300	30	65.90	22.52	1.222	80.60	
SPF shaving							Peng et al. [21]
Raw				18.13			
Torrefied	240	60	86.7	20.89	1.152	90.89	
	270	60	66.2	23.11	1.275	76.81	

Table 4 (continued)

Biomass	T (°C)	t (min)	SY ^a (%)	HHV ^b (MJ kg ⁻¹)	EF ^c (–)	EY ^d (%)	Reference
	300	60	49.3	25.32	1.397	62.72	
	300	60	39.4	29.49	1.627	58.33	

^a Solid yield.^b Higher heating value.^c Enhancement factor in HHV.^d Energy yield.**Table 5**
Properties of untreated and torrefied biomass and coal.

Material	Volatile matter (wt%)	Fixed carbon (wt%)	Higher heating value (MJ kg ⁻¹)
Raw biomass	67–88	0.5–20	15–20
Torrefied biomass	34–85	13–45	16–29
Coal	0.5–50	46–92	25–35

Biomass is hygroscopic in nature because moisture can be absorbed into the cell walls and hydrogen-bonded to the hydroxyl groups of the cell wall components [36]. In general, the moisture content in biomass ranges from 30 to 60 wt%, depending on type, location, time of harvest and period of storage after harvest [34]. Recent studies [19,37–40,20–22] suggest that torrefaction changes the hygroscopic nature of biomass to hydrophobic so that the saturated moisture content in biomass is reduced significantly. For example, in the study of Felfri et al. [19], the equilibrium moisture in briquettes was approximately reduced by 73% after torrefaction. The study of Sadaka and Negi [37] indicated that the equilibrium moisture content in wheat straw, rice straw and cotton gin waste after torrefaction at 260 °C for 1 h were reduced by 70.5, 49.4 and 48.6 wt%, respectively. The hydrophobic characteristic of torrefied biomass can also be observed in TGA curves where its weight loss is slighter for heating temperatures between room temperature and 100 °C when compared to its parent materials [41]. On the other hand, the study of Li et al. [20] indicated that the hydrophobicity of the torrefied sawdust was enhanced with increasing the severity of treatment.

When biomass undergoes torrefaction, the hydroxyl groups will be partly destroyed through dehydration [38]. This prevents the formation of hydrogen bonding [42] so that the torrefied biomass becomes hydrophobic. The lower saturated moisture content in torrefied biomass could also result from tar condensation inside the pores, obstructing the passage of moist air through the solid, and then avoiding the condensation of water vapor. The apolar character of condensed tar on the solid also prevents the condensation of water vapor inside the pores [19].

3.3.2. Volatile matter, fixed carbon and elemental contents

Apart from saturated moisture content, the proximate analysis of biomass also reveals the properties changes in volatile matter (VM), fixed carbon (FC), and ash after torrefaction. Table 3 lists the VM and FC contents, the atomic oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios as well as the higher heating values (HHVs) of a variety of biomass species after torrefaction. As can be seen in the table, the VM content of raw biomass is high, ranging from 70 to 88 wt%, while its FC content is low, ranging from 10 to 21 wt%. By virtue of the dehydration process of biomass from torrefaction [5], moisture and light volatiles are liberated from the materials. Therefore, VM in biomass is decreased, whereas FC is increased. The VM and FC contents of torrefied biomass are approximately in the ranges of 40–85 wt% and 13–45 wt%, respectively. Fig. 4a demonstrates the profiles of VM and FC of biomass before and after torrefaction, which clearly depicts the linear decrease of VM with increasing FC.

The main elements in biomass include carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S). Carbon in a fuel is the major source of heat released from combustion. Hydrogen is also an important source of heat in combustion; however, more hydrogen contained in a fuel is usually accompanied by a lower content of carbon. Oxygen contained in biomass is conducive to fuel burning, but it reduces the calorific value of biomass.

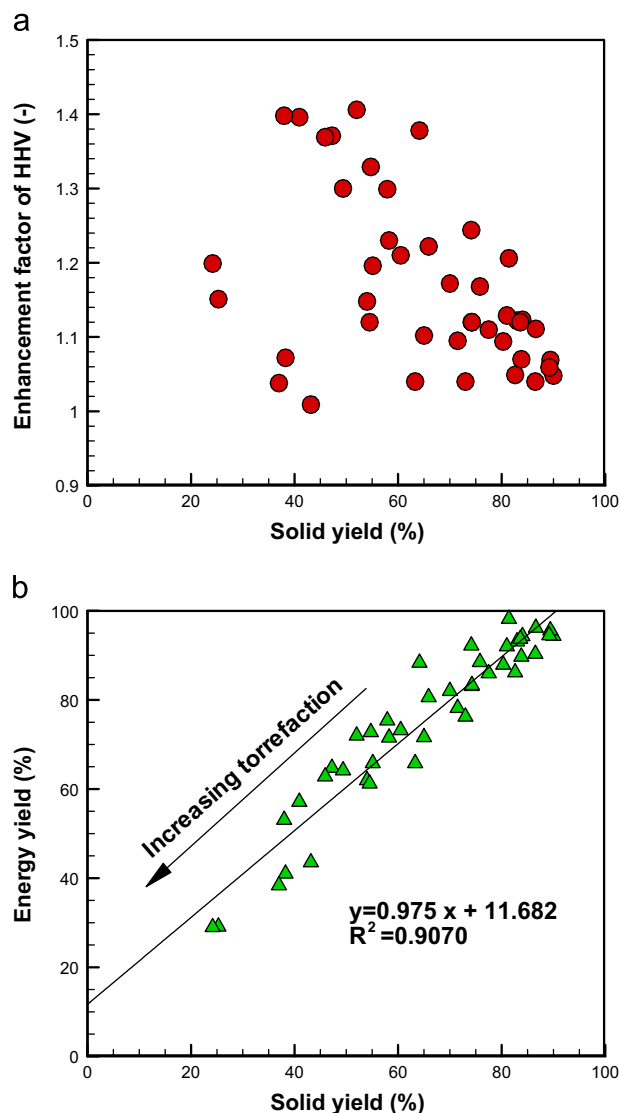
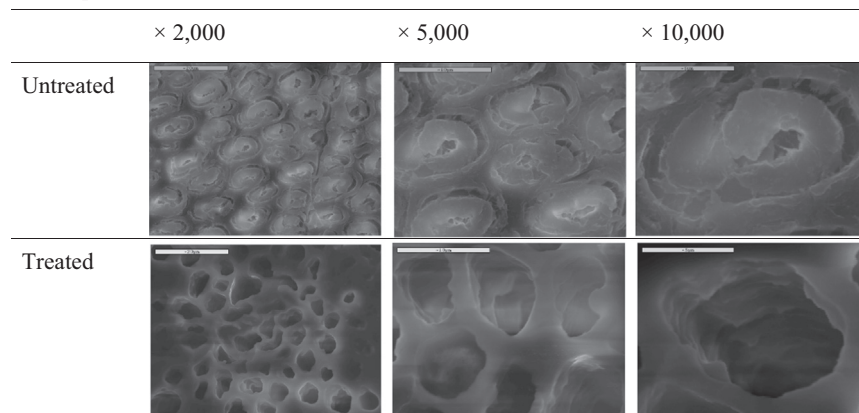
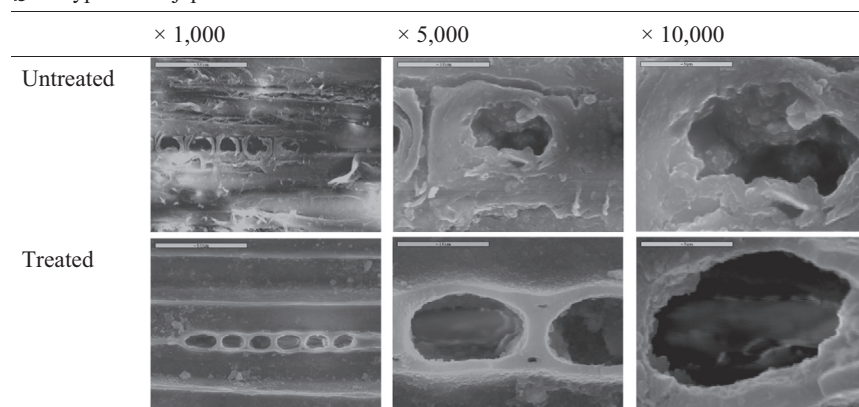
**Fig. 5.** The plots of (a) solid yield versus the enhancement factor of HHV and (a) solid yield versus energy yield of various biomass species.

Table 6
Correlations of the HHV of biomass.

Correlation (HHV, MJ kg ⁻¹)	Reference
HHV ^a =0.3536FC+0.1559VM–0.0078Ash	Parikh et al. [49]
HHV ^a =0.3491C+1.1783H+0.1005S–0.1034O–0.0151N–0.0211Ash	Channiwala and Parikh [51]
HHV ^b =0.0893L ^c +16.9742 (for wood biomass)	Demirbaş [52]
HHV ^b =0.0877L ^c +16.4951 (for non-wood biomass)	Demirbaş [52]
HHV ^a =0.2949C+0.8250H	Yin [50]
HHV ^a =0.2521FC+0.1905VM	Yin [50]

^a Dry basis (wt%).^b Dry-ash-free and extractive-free basis (wt%).^c Lignin (wt%).**a** Oil palm fiber**b** *Cryptomeria japonica***Fig. 6.** SEM images of (a) oil palm fiber and (b) *Cryptomeria japonica* before and after torrefaction.

The higher the oxygen and ash contents in a fuel, the lower the heating value. Compared to coal, carbon, nitrogen and sulfur contents in biomass are low, whereas its hydrogen and oxygen contents are high. Moreover, the moisture content in biomass is usually higher than that in coal. As a result, the calorific value of biomass is lower than that of coal.

In general, the atomic oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios in raw biomass are in the ranges of 0.4–0.8 and 1.2–2.0, respectively. After undergoing torrefaction, moisture and light volatiles, which contain more hydrogen and oxygen, are removed from biomass, whereas relatively more carbon is retained. This results in the slight or mild carbonization of biomass. As a consequence, the atomic O/C and H/C ratios are decreased to 0.1–0.7 and 0.7–1.6, respectively. The van Krevelen diagram for the biomass species listed in Table 3 is shown in Fig. 4b. The atomic H/C ratio and the atomic O/C ratio follow approximately a linear relationship. Compared to coal, the sulfur

content in biomass is much lower. Therefore, much less sulfur oxides are emitted into the atmosphere when biomass is burned. In recent studies [43], it was found that sulfur contained in biomass was also reduced after torrefaction.

3.3.3. Solid yield, energy density and energy yield

When biomass is torrefied, its dry matter is lost because of the thermal degradation. The solid yield is defined as the mass ratio of torrefied biomass and its parent biomass, with the value being less than unity. The solid yields and HHVs of a variety of raw and torrefied biomass materials at various operating conditions are listed in Table 4. The table suggests that some biomass species are not suitable for torrefaction. For example, when rape stalk [44] and empty fruit bunches [45] are torrefied at 300 °C for 30 min, their solid yields are merely 25.3% and 24.2%, respectively, compared to the typical solid yield of 50–90%, as shown in Table 4.

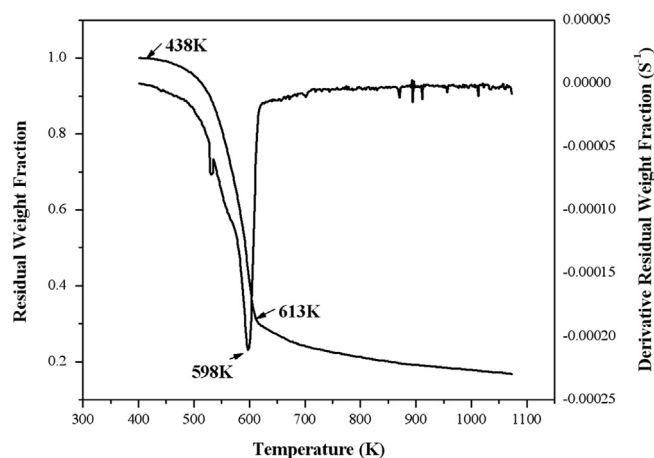


Fig. 7. Dynamic TG curves of pine wood [6].

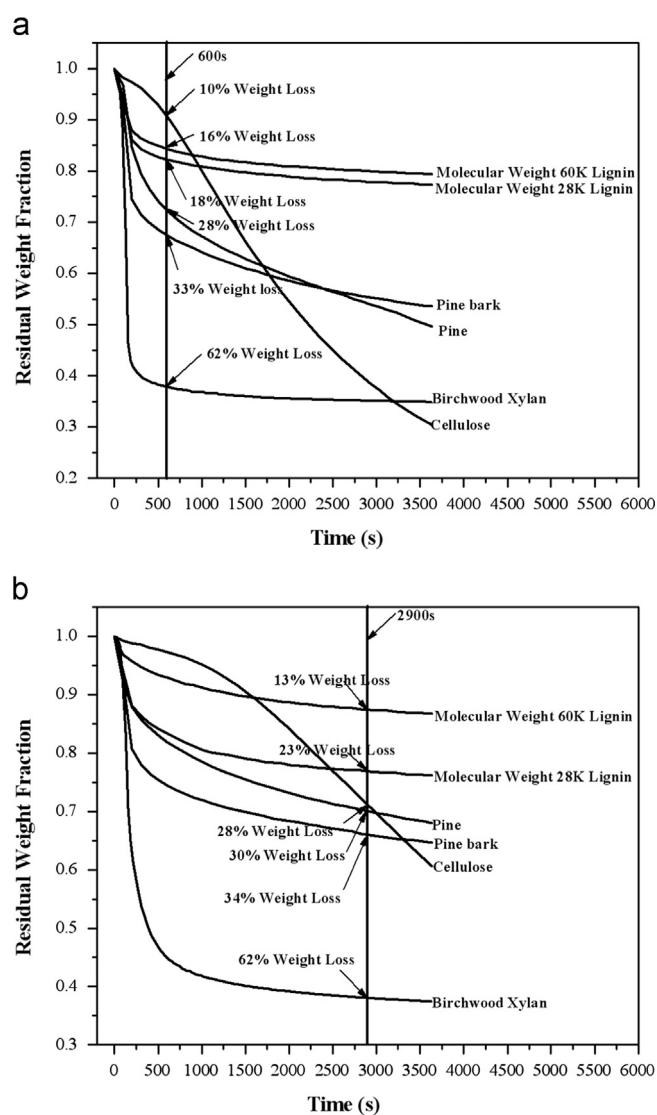


Fig. 8. Isothermal TG curves of British Columbia pine, pine bark and three major components. (a) 300 °C, (b) 280 °C [6].

Intensifying the calorific value or energy density of solid biomass fuel is the prime goal of torrefaction. The higher heating values (HHVs) of raw biomass and coal are generally in the ranges of 15–20 and 25–35 MJ kg⁻¹, respectively. Consequently, it is

essential to enhance the energy density of biomass if it is used as an alternative to coal. Tables 3 and 4 indicate that the HHV of torrefied biomass is approximately between 16 and 29 MJ kg⁻¹ which is closer to the HHV of coal. The volatile and fixed carbon contents and HHVs of untreated and torrefied biomass and coal are tabulated in Table 5. An enhancement factor can be defined as the HHV ratio between torrefied biomass and raw biomass, with the factor being always larger than unity. Fig. 5a shows the enhancement factor of HHV as a function of solid yield based on the data listed in Table 4. The figure depicts that the enhancement factor can reach up to 1.4.

The energy yield is defined by the energy content ratio between torrefied biomass and its raw biomass, which is equivalent to the multiplication of the solid yield and the enhancement factor of HHV [46,47]. The study of Almeida et al. [48] and Peng et al. [22] indicated that the calorific value of a material decreased almost linearly with increasing torrefaction mass loss. The plot of energy yield versus solid yield in Fig. 5b suggests that a decrease in solid yield linearly decreases the energy yield of biomass, even though the enhancement factor of HHV is enlarged (Fig. 5a).

In the past, a number of correlations in terms of proximate [49,50], elemental [50,51] or fiber [52] analysis have been developed to predict the HHV of raw biomass. The correlations are tabulated in Table 6. The correlations suggest elemental carbon and hydrogen or fixed carbon as the main sources of calorific value. Although the elemental hydrogen and volatile matters in biomass are reduced from torrefaction, elemental carbon is increased markedly which results in the intensification of the HHV of biomass. Past studies [10,53] have shown that those correlations developed for raw biomass are also applicable to the prediction of the HHV of torrefied biomass.

3.3.4. Grindability

Coal has been extensively used in industry as a fuel. Before coal is burned in boilers or blast furnaces, it has to be pulverized to facilitate injection and fast combustion. The pulverization of coal is an energy intensive process. If biomass is burned in boilers and blast furnaces alone or blended with coal for co-firing, it has to be ground as well [54–57]. In lignocellulosic biomass, cellulose microfibrils are embedded in a matrix of hemicelluloses, with hemicellulose and cellulose being densely packed by layers of lignin [58,59]. After biomass is torrefied, a portion of hemicellulose is removed and the cell walls in biomass are destroyed. Fig. 6 demonstrates the scanning electron microscope (SEM) images of oil palm fiber and *Cryptomeria japonica* before and after torrefaction (at 300 °C for 1 h) [60]. There are plentiful inclusions in the thick-walled fibers of raw oil palm fiber (Fig. 6a). After undergoing torrefaction, a lot of inclusions disappear and the tubular structure is more clearly exhibited. Similar to oil palm fiber, the cells in *Cryptomeria japonica* are filled with inclusions (Fig. 6b). When the biomass is torrefied, the inclusions are removed drastically as clearly exhibited by the cell structures. This change in microstructure gives rise to the improved grindability of torrefied biomass. The improved grindability of biomass leads to the increase in weight percentages of fine particles under the same grinding conditions [61,9]; it also reduces the specific energy consumption for grinding torrefied wood chips by up to 90% compared to raw wood chips [39]. Ohliger et al. [29] reported that the grindability of beechwood in terms of hardgrove grindability index (HGI) as well as in terms of crushing ratio increased almost monotonously with the mass loss of the solid during torrefaction.

3.3.5. Reactivity, particle size distribution and surface area

Biomass is an abundant resource in nature. However, the biomass sources are diverse and some residual biomass is highly

heterogeneous, making their energy use rather difficult. When biomass is used as a fuel or feedstock, its quality depends on the types of raw biomass, climatic variation, harvest season, and storage conditions. This variability in biomass significantly affects its utility as a fuel, resulting from its non-uniform properties. Once biomass is torrefied, most of the moisture as well as part of the volatiles and hemicellulose in biomass are removed. Therefore, torrefaction produces more uniform feedstocks of consistent quality. This makes the control of burning biomass or the use as a feedstock easier. Bridgeman et al. [62] exposed raw and torrefied willow to a methane-air flame in their experiments and found that the torrefied willow ignited more quickly, presumably because of its low moisture content and improved reactivity. The combustion behavior of both raw and torrefied rice husks in a spout-fluid bed combustor was studied by Pimchuai et al. [63] by measuring its temperature history at different zones. It was observed that torrefied husks were ignited faster and the bed temperature was raised to a higher level because of its low moisture content.

Particle size distribution and surface area are two important parameters for evaluating the flowability and combustion behavior of a fuel for its utility. The study of Phanphanich and Mani [39] concerning torrefied pine chips and logging residues indicated that the curves of particle size distribution shifted toward the smaller particle sizes with increasing torrefaction temperature. The study of Chen et al. [41] showed that more small particles were generated from the comminution of torrefied Lauan when the torrefaction duration increased. Chen et al. [10] also investigated the particle size variations of pulverized bamboo, banyan and willow before and after torrefaction. Before torrefaction, smaller particles were featured by agglomeration, especially for banyan and willow where the double-peak distributions were observed. After torrefaction, the tendency for agglomeration was eliminated and the particle size distribution became more uniform. With regard to particle surface area, Phanphanich and Mani [39] found that the surface areas of torrefied pine chips and logging residues were higher than those of their parent biomass. However, the study of Rousset et al. [64] revealed that torrefaction had no effect on the surface area of babassu shells. This might be due to the sensitivities of various biomass species to heat treatment in different reactors used by different researchers.

3.4. Torrefaction kinetics

Pyrolysis kinetics has been well studied and documented. Several review papers have been published on the reaction mechanisms and the kinetic models for biomass pyrolysis [67–71,4,5]. Some of those

pyrolysis models may thus be extended for torrefaction, a mild pyrolysis at temperatures below 327 °C.

The weight loss of wood and its chemical compositions started at 250 °C [72]. Between 250 and 300 °C, the weight loss was caused by dehydration reactions via bond scission with the elimination of H₂O, carbonyl and carboxyl group formation reactions with the elimination of CO and CO₂, and limited devolatilization and carbonization for the production of final tars and chars [73]. At temperatures above 300 °C, the extensive devolatilization involving free radical cleavage of the glucosidic bond (the formation of tars and gases) and the extensive carbonization involving the formation of intermediate carbonium ions (the formation of chars) became dominant. As shown in Fig. 7, significant weight loss of pine started at 165 °C (438 K). The rate of weight loss was steady, and reached a peak at around 325 °C (598 K), which corresponds to the maximum decomposition rate. The weight loss inflection point of pine was 340 °C (613 K), and beyond the inflection point the weight loss rate decreased.

Most researchers suggested that the weight loss of wood during torrefaction was from the decomposition of hemicelluloses, followed by cellulose and lignin [74]. Peng et al. [6] observed that at a torrefaction temperature of 300 °C with a reaction time of 600 s, the weight losses of xylan, cellulose and lignin were 62%, 10% and 18%, respectively, and the weight loss of wood during torrefaction could be approximately estimated from the weight loss data of pure cellulose, hemicelluloses, and lignin in wood species, as shown in Fig. 8.

3.4.1. One-step kinetics

The simplest kinetic model for torrefaction of wood and its components is the one-step kinetic model.



The overall reaction equations for the one-step kinetic model with n^{th} order torrefaction reaction can be written as

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n$$

Table 7 gives a summary of one-step model reaction kinetic constants for wood torrefaction. The activation energy varies widely from 88 to 174 kJ/mol under different heating conditions, using different experimental devices (TGA, tube furnaces, entrained and fluid bed reactors, screen heaters, and drop tubes) and samples of different characteristics (size, mass, and wood species), and applying different mathematical treatment methods for the experimental data.

Table 7
One-step torrefaction model reaction constants for wood.

Materials	n	Operating conditions	Reaction rates, s^{-1}	Sources
Whatman	0.5	TGA, 200–400 °C, 1.5 K/min, N ₂	$k = 2.1 \times 10^{11} \exp(-153,000/RT)$	Rogers et al. [75]
Oak, 650 μm	1	Isotherm tube furnace, 300–400 °C	$k = 2.5 \times 10^6 \exp(-106,500/RT)$	Thurner et al. [76]
Wild cherry	1	Isotherm tube furnace, 265–320 °C	$k = 1.2 \times 10^{12} \exp(-173,700/RT)$	Ward et al. [77]
Pine	1	TGA, 150–500 °C, 5 K min ⁻¹	$k = 5.0 \times 10^8 \exp(-88,000/RT)$	Gronli et al. [78]
Epicea	1		$k = 1.6 \times 10^6 \exp(-92,000/RT)$	
Hetre	0.01	TG, dynamic, 20–400 °C, 5 K min ⁻¹	$k = 7.7 \times 10^9 \exp(-111,000/RT)$	Avat [79]
Pine, 100–125 μm	1	TGA drop tube, 280–400 °C	$k = 1.4 \times 10^{10} \exp(-150,000/RT)$	Wagenaar et al. [80]
Forest waste, < 1000 μm ,	1	Isotherm TGA, 225–325 °C	$k = 7.7 \times 10^7 \exp(-124,870/RT)$	Reina et al. [81]
Beech, < 80 μm , 9 mg	1	Tube furnace, 300–435 °C	(a) $k = 2.4 \times 10^5 \exp(-95,400/RT)$ (b) $k = 4.4 \times 10^9 \exp(-141,000/RT)$	Blasi et al. [82]
Pine	1	Isotherm TGA, 200–300 °C	$k = 2.9 \times 10^8 \exp(-130,690/RT)$	Peng et al. [6]
Fir	1	Isotherm TGA, 250–300 °C	$k = 1.6 \times 10^8 \exp(-127,920/RT)$	
Spruce	1	Isotherm TGA, 230–300 °C	$k = 2.6 \times 10^5 \exp(-94,920/RT)$	
SPF	1	Isotherm TGA, 250–300 °C	$k = 4.3 \times 10^7 \exp(-12,240/RT)$	
Pine bark	1	Isotherm TGA, 250–300 °C	$k = 5.8 \times 10^2 \exp(-69,410/RT)$	

Table 8 shows some determined one-step first order reaction kinetics model equations for torrefaction of cellulose, hemicelluloses, and lignin.

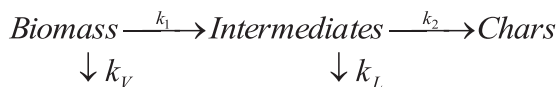
It was reported [6] that the one-step kinetic model could predict the torrefaction reaction reasonably well over the long residence time, but poorly over the short residence time with a low weight loss during torrefaction.

3.4.2. Multi-step kinetics

The multi-step kinetic model was used for biomass pyrolysis to predict the reaction rates and the product yields. For wood pyrolysis, Branca and Blasi [94] proposed a three-step kinetic model based on three reactions at different temperature ranges: depolymerization (255–320 °C), devolatilization (255–435 °C), and charring (330–435 °C).

For wood torrefaction, Prins et al. [74] assumed that the weight loss of biomass during torrefaction was primarily from the decomposition of hemicelluloses, and suggested that the Blasi

and Lanzetta [95] model, a two-step kinetic model, was used.



Volatiles

Volatiles

If all torrefaction reactions are assumed to be first order, the residual weight fraction (W_{TGA}) of cellulose can be expressed as

$$W_{TGA} = \left(1 + \frac{[K_1 K_1 - k_1 k_2]}{[K_1 (K_2 - K_1)]}\right) e^{-K_1 t} + \left[\frac{-k_1 K_2 + k_1 k_2}{K_2 (K_2 - K_1)}\right] e^{-K_2 t} + \frac{k_1 k_2}{K_1 K_2}$$

where

$$K_1 = k_1 + k_V$$

$$K_2 = k_2 + k_L$$

3.4.3. Multi-components kinetics

The dynamic TG curves of wood and its components show overlapped peaks for the decomposition of cellulose, hemicelluloses, and

Table 8

One-step torrefaction model reaction constants for biomass components.

Operating conditions	Reaction rates, s ⁻¹	Sources
Cellulose		
TGA, 200–460 °C, 3 K min ⁻¹	$k = 4.3 \times 10^{12} \exp(-242,400/RT)$	Tang et al. [83]
TGA, 0.23–5 K min ⁻¹	$k = 6.6 \times 10^{16} \exp(-224,000/RT)$	Akita et al. [84]
TGA, 7 K min ⁻¹	$k = 2.4 \times 10^{20} \exp(-248,000/RT)$	Fairbridge et al. [85]
TGA, 260–290 °C, isothermal	$k = 1.8 \times 10^{11} \exp(-113,000/RT)$	Bilbao et al. [86]
TGA, 200–500 °C, 5 K min ⁻¹	$k = 3.8 \times 10^{21} \exp(-260,000/RT)$	Williams et al. [87]
80 K min ⁻¹	$k = 9.6 \times 10^{14} \exp(-188,000/RT)$	
TGA, 177–427 °C, 5 K min ⁻¹	$k = 4.0 \times 10^7 \exp(-89,000/RT)$	Orfao et al. [88]
TGA, 200–300 °C isothermal	$k = 2.9 \times 10^9 \exp(-124,420/RT)$	Chen and Kuo [89]
TGA, 280–300 °C isothermal	$k = 1.7 \times 10^{19} \exp(-213,540/RT)$	Peng et al. [6]
Hemicelluloses		
Isothermal glass bulb reactor, 110–220 °C	$k = 1.3 \times 10^{14} \exp(-111,000/RT)$	Stamm [90]
Isothermal TGA, 215–250 °C	$k = 7.8 \times 10^{12} \exp(-125,000/RT)$	Ramiah [91]
TGA, 240–250 °C, 5 K min ⁻¹	$k = 1.7 \times 10^{20} \exp(-119,000/RT)$	Hirata [92]
Ceramic tube, up to 560 °C, 30 K min ⁻¹	$k = 5.2 \times 10^{12} \exp(-124,000/RT)$	Min [93]
TGA, 200–400 °C, 1.5 K min ⁻¹	$k = 3.5 \times 10^4 \exp(-43,000/RT)$	Bilbao et al. [86]
20 K min ⁻¹	$k = 7.2 \times 10^7 \exp(-72,000/RT)$	
80 K min ⁻¹	$k = 2.7 \times 10^9 \exp(-86,000/RT)$	
TGA, up to 720 °C, 5 K min ⁻¹	$k = 6.7 \times 10^{25} \exp(-258,000/RT)$	Williams et al. [80]
20 K min ⁻¹	$k = 9.6 \times 10^7 \exp(-257,000/RT)$	
40 K min ⁻¹	$k = 1.1 \times 10^{19} \exp(-194,000/RT)$	
80 K min ⁻¹	$k = 5.8 \times 10^{12} \exp(-125,000/RT)$	
Isothermal TGA, 280–300 °C	$k = 1.4 \times 10^{11} \exp(-145,500/RT)$	Peng et al. [6]
Lignin		
TGA, 280–344 °C	$k = 5.9 \times 10^7 \exp(-87,800/RT)$	Tang [83]
TGA, 250–500 °C, 5 K min ⁻¹	$k = 1.5 \times 10^{11} \exp(-124,000/RT)$	Williams et al. [87]
TGA, 200–300 °C isothermal	$k = 6.6 \exp(-37,580/RT)$	Chen and Kuo [9]
TGA, 280–300 °C isothermal	$k = 5.0 \times 10^3 \exp(-76,050/RT)$	Peng et al. [6]

Table 9

Three-component pyrolysis model reaction rate constants for wood.

Materials	Operating conditions	Reaction rate constant, s ⁻¹	Sources
Cellulose	TGA, 200–500 °C, 5 K min ⁻¹ , N ₂	$k = 6.3 \times 10^{19} \exp(-260,000/RT)$	Williams et al. [87]
Cellulose	80 K min ⁻¹ , N ₂	$k = 1.6 \times 10^{13} \exp(-188,000/RT)$	
Hemicelluloses	5 K min ⁻¹	$k = 2.1 \times 10^{22} \exp(-259,000/RT)$	
Hemicelluloses	80 K min ⁻¹ , N ₂	$k = 1.6 \times 10^9 \exp(-125,000/RT)$	Orfao et al. [88]
Lignin	5 K min ⁻¹	$k = 2.5 \times 10^9 \exp(-124,000/RT)$	
Cellulose	TG, dynamic, 177–427 °C,	$k = 6.6 \times 10^5 \exp(-89,000/RT)$	
Hemicelluloses	5 K min ⁻¹ , N ₂	$k = 1.1 \times 10^5 \exp(-198,000/RT)$	
Lignin		$k = 5.3 \times 10^{14} \exp(-18,100/RT)$	

Table 10

Two-component torrefaction reaction rate constants for wood [6].

Items	C ₁	C ₂	Reaction rate constants, s ⁻¹	
Pine	0.263	0.704	$k_1 = 1.2 \times 10^8 \exp(-115,000/RT)$	$k_2 = 4.3 \times 10^{16} \exp(-225,000/RT)$
Fir	0.250	0.722	$k_1 = 3.0 \times 10^7 \exp(-110,000/RT)$	$k_2 = 1.3 \times 10^{18} \exp(-241,000/RT)$
Spruce	0.200	0.775	$k_1 = 2.9 \times 10^{10} \exp(-140,000/RT)$	$k_2 = 1.8 \times 10^{13} \exp(-187,000/RT)$
Pine bark	0.179	0.672	$k_1 = 1.4 \times 10^4 \exp(-66,000/RT)$	$k_2 = 1.1 \times 10^5 \exp(-97,500/RT)$

lignin for weight loss over a wide temperature range [96,6]. By assuming that the weight loss is contributed from the decomposition of the three major organic pseudo-components in temperature ranges, the overall reaction rate is expressed as a linear combination of these component reactions:

$$\frac{\partial w^{calc}}{\partial t} = - \sum_{j=1}^M C_j \frac{\partial \alpha_j}{\partial t}$$

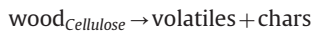
$$\frac{\partial \alpha_j}{\partial t} = k_j (1 - \alpha_j)^{n_j}$$

$$k_j = A_j e^{-E_{aj}/RT}$$

where α_j is defined as the conversion, and d_{α_j}/dt is the reaction rate of pseudo-component j .

Wood typically contains 20–30% hemicelluloses, 28–38% cellulose, and 10–15% lignin. Table 9 shows the reported reaction rate constants for the first order reactions of pseudo-hemicelluloses, pseudo-cellulose, and pseudo-lignin in the literature.

Based on the observation that the hemicelluloses decompose quickly in wood pyrolysis, Roberts [97] proposed a two-component kinetics model for wood pyrolysis,



Similarly, a two-component torrefaction reaction kinetic model was developed by Peng et al. [6] for biomass torrefaction within short residence time



By assuming first order reactions for both components, the residual weight fraction (W_{TGA}) of wood samples is given by

$$W_{TGA} = (1 - C_1 - C_2) + C_1 \exp(-A_1 e^{-E_1/RT} t) + C_2 \exp(-A_2 e^{-E_2/RT} t)$$

where C_1 and C_2 represent the contents of component 1, mostly hemicelluloses, and component 2, mostly the combined cellulose and lignin.

The estimated two-component torrefaction kinetic constants for BC softwood samples as estimated by regression of isothermal TG data at a reaction time less than 2 h are shown in Table 10. The two-component torrefaction model was found to give a better agreement with the isothermal TG data over the short residence time range than the single-component model [6].

3.4.4. Particle size effect

Although the reaction temperature and reaction residence time are the most influential parameters, particle size also affects the torrefaction reaction rate because of the diffusion of generated vapors through internal pores of biomass particles. Prins et al. [74] postulated that for pyrolysis of wood below 300 °C, the reaction was the rate-limiting step for particles smaller than 2 mm where

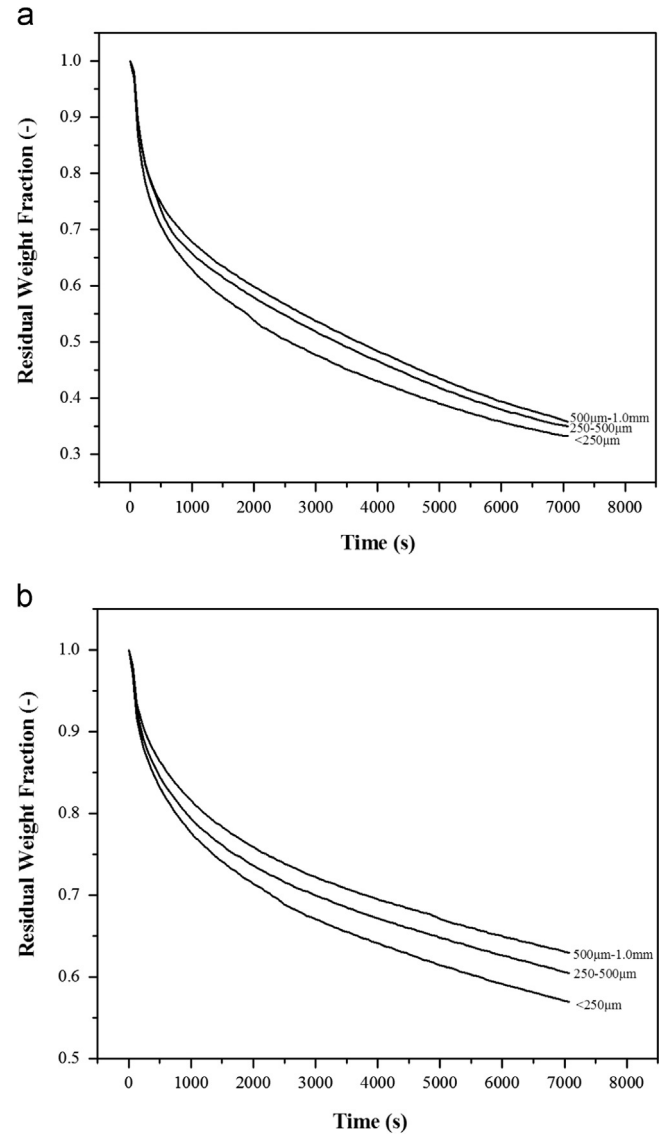


Fig. 9. Weight loss curves of three pine sawdust samples of different sizes in a TGA. (a) 300 °C and (b) 280 °C [17].

the impact of intra-particle heat and mass transfer became insignificant. Peng et al. [17] observed that the overall torrefaction rate was still affected by the particle size even for particles smaller than 1 mm, especially at high temperatures (see Fig. 9), which was attributed to the internal diffusion of generated vapors through those newly created micropores inside biomass particles.

Based on the fitting of a series of TGA and fixed bed experimental data, the hard core or non-shrinkage particle model with a first order torrefaction reaction model was found to give a good fit to the data, and the global reaction rate was found to be inversely proportional to the particle size to a power of 0.24.

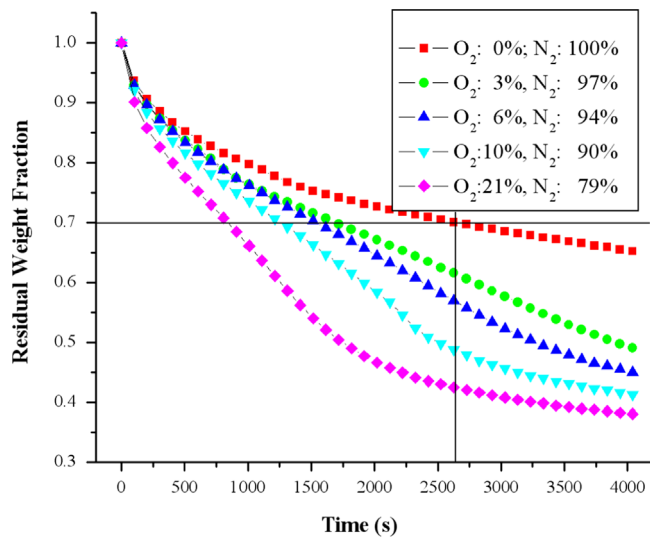
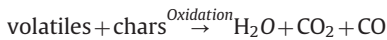
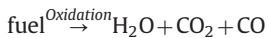


Fig. 10. TG curves of pine particles using carrier gas at different oxygen concentrations [99].

3.4.5. Oxygen effect

Senneca et al. [98] suggested that the low-temperature oxidation of solid fuel has two parallel pathways. One is the direct burning of the pure solid fuel and the second is the oxidation of chars and volatiles produced by pyrolysis.



Senneca et al. [99] further proposed a power law kinetics model for the oxidative pyrolysis of solid fuels based on fitting the weight loss TG curves with carrying gas containing 5–21% oxygen:

$$\frac{dx}{dt} = -k_{0,0_2} \exp\left(-\frac{E_{O_2}}{RT}\right) x^m P_{O_2}^n$$

where x is the solid conversion (dry basis), t is the reaction time, $k_{0,0_2}$ is the pre-exponential factor of oxidation, E_{O_2} is the activation energy of oxidation, m is the reaction order with the partial pressure of oxygen, T is the reaction temperature, P_{O_2} is the partial pressure of oxygen level in the atmosphere, n is the oxygen effect reaction order.

Uemura et al. [45] suggested that the torrefaction reaction kinetics of oil palm empty fruit bunches (EFB) in the presence of 0–21% oxygen concentration followed two parallel pathways. One is the hemicelluloses decomposition which represents the original torrefaction reaction, and the other is the biomass oxidation.

$$-r_{\text{overall}} = (-r_{\text{torrefaction}}) + (-r_{\text{oxidation}}) = k_{\text{torrefaction}} C_{\text{HC}}^l + k_{\text{oxidation}} C_{\text{EFB}}^m C_{O_2}^n$$

where $-r_{\text{overall}}$ is the reaction rate of EFB, $-r_{\text{torrefaction}}$ is the torrefaction reaction rate of EFB, $-r_{\text{oxidation}}$ is the oxidation reaction rate of EFB, $k_{\text{torrefaction}}$ is the torrefaction reaction rate constant, $k_{\text{oxidation}}$ is the oxidation reaction rate constant, HC is the hemicelluloses concentration in EFB, CEFB is the EFB concentration, CO_2 is the oxygen concentration, l is the torrefaction reaction order, m is the reaction order with the partial pressure of oxygen, and n is the oxygen effect order.

Wang et al. [100] investigated the oxidative torrefaction of pine particles with different oxygen concentrations in the carrier gas, found that the oxygen level in the carrier gas affected the weight

loss significantly (see Fig. 10), and subsequently developed a two-component kinetic model for the oxidative torrefaction.

$$-r_{\text{overall}} = (-r_{\text{torrefaction}}) + (-r_{\text{oxidation}})$$

$$-r_{\text{torrefaction}} = (-r_{\text{fast group torrefaction}}) + (-r_{\text{medium group torrefaction}})$$

$$-r_{\text{oxidation}} = (-r_{\text{fast group oxidation}}) + (-r_{\text{medium group oxidation}})$$

$$r_{\text{fast group torrefaction}} = \frac{dr_{\text{fast group torrefaction}}}{dt} = -k_1 \times C_{\text{fast group}}$$

$$r_{\text{medium group torrefaction}} = \frac{dr_{\text{medium group torrefaction}}}{dt} = -k_2 \times C_{\text{medium group}}$$

$$r_{\text{fast group oxidation}} = \frac{dr_{\text{fast group oxidation}}}{dt} = -k'_{O_1} \times C_{\text{fast group}}^{m_1} \times C_{O_2}^{n_1} = -k_{O_1} \times C_{\text{fast group}}^{m_1} \times y_{O_2}^{n_1}$$

$$r_{\text{medium group oxidation}} = \frac{dr_{\text{medium group oxidation}}}{dt} = -k'_{O_2} \times C_{\text{medium group}}^{m_2} \times C_{O_2}^{n_2} = -k_{O_2} \times C_{\text{medium group}}^{m_2} \times y_{O_2}^{n_2}$$

where $C_{\text{fast group}}$ is the fast reaction group weight fraction, $C_{\text{medium group}}$ is the medium reaction group weight fraction, y_{O_2} is the oxygen mole fraction, k_{O_1} ($=k'_{O_1} C_{O_2}^{n_1}$) is the lumped oxidation reaction rate constant of the fast reaction group, k_{O_2} ($=k'_{O_2} C_{O_2}^{n_2}$) is the lumped oxidation reaction rate constant of the medium reaction group, m_1 and m_2 are the oxidation reaction order for the fast reaction group and the medium reaction group, and n_1 and n_2 are the oxygen reaction order for the fast reaction group and the medium reaction group, respectively.

If the two oxidation reactions are assumed to be first order reactions with respect to the biomass concentration and the oxygen is in excess amount in the TG test, the residual weight fraction (W_{TGA}) of softwood samples is given by

$$W_{\text{TGA}} = (1 - C_1 - C_2) + C_1 \exp[-(k_1 + k_{O_1} \times y_{O_2}^{n_1})t] + C_2 \exp[-(k_2 + k_{O_2} \times y_{O_2}^{n_2})t]$$

Based on the isothermal TG weight loss curves (Fig. 10), the following kinetic parameters were obtained.

$$\begin{aligned} k_1 &= 5.4 \times 10^{10} \exp(-145,900/RT), \text{ s}^{-1}; \\ k_2 &= 2.3 \times 10^{11} \exp(-168,600/RT), \text{ s}^{-1}; \\ k_{O_1} &= 4.9 \times 10^5 \exp(-86,600/RT), \text{ s}^{-1}; \\ k_{O_2} &= 1.7 \times 10^{11} \exp(-153,400/RT), \text{ s}^{-1}; \\ n_1 &= 1.0; \\ n_2 &= 0.69. \end{aligned}$$

3.5. Oxidative, wet and steam torrefaction

In addition to non-oxidative or conventional torrefaction, namely, biomass torrefied in an inert or non-oxidative environment, biomass torrefaction can also be carried out under other environments, such as oxygen-containing gases, high pressure water or steam, as explored in recent years by some researchers. They provide an alternate approach to upgrade solid biomass.

3.5.1. Oxidative torrefaction

Non-oxidative torrefaction is able to upgrade biomass; however, additional operating costs from heating and inert gas (usually nitrogen) supply are incurred. A reduction in cost could potentially be achieved if torrefaction is carried out in oxidative atmospheres. Oxidative torrefaction means that biomass is torrefied in an environment containing oxygen with the temperature in the same range of 200–300 °C. If air or combustion flue gas is utilized as a carrier gas, the process of gas separation for extracting nitrogen is no longer needed. In contrast to non-oxidative torrefaction where

the main mechanisms include devolatilization and thermal degradation of biomass [101], oxidative reactions also occur in oxidative torrefaction [102,103,66,100,104]. The accompanied oxidative reactions in oxidative torrefaction are usually exothermic, implying that heat can be generated from the reactions. This also reduces the heating demand for the endothermic biomass torrefaction reactions. Besides, the reaction rates of oxidative torrefaction are generally faster than those of thermal pyrolysis; this will shorten the torrefaction duration. The studies of Wang et al. [100], Calvo et al. [105], Fang et al. [106], and Chiang et al. [107] suggested that an increase in O_2 concentration could result in a higher decomposition rate of biomass, leading to shortened torrefaction time or lowered torrefaction temperature to achieve a targeted weight loss.

Lu et al. [11] recently evaluated the properties of eucalyptus and oil palm fiber pretreated in N_2 and air atmospheres (0 and 21 vol% of O_2) at temperatures of 250–350 °C for 1 h. They pointed out that it was feasible to upgrade eucalyptus in N_2 and air atmospheres at temperatures of 325 and 275 °C, respectively; but it was inappropriate to torrefy oil palm fiber in air, resulting from low solid and energy yields. Rousset et al. [108] investigated the property variation of *Eucalyptus grandis* in oxidative environments. Two torrefaction temperatures of 240 and 280 °C and four O_2 concentrations of 2, 6, 10 and 21 vol% were taken into account, and the biomass was torrefied for 1 h. They reported that the O_2 concentration did not substantially affect the solid yield and composition of the biomass torrefied at 240 °C. The influence of increasing O_2 concentration on solid yield reduction and compositional change at 280 °C was more than that at 240 °C, but it was significant only at the O_2 concentration of 21 vol%. Uemura et al. [109] explored the effects of temperature (220, 250, and 300 °C), oxygen concentration (0, 3, 9 and 15 vol%), and biomass size (0.375, 1.5, 3 and 6 mm) on the solid and energy yields of oil palm empty fruit bunches. Similar to temperature, an increase in O_2 concentration decreased the solid and energy yields in their study, but the yields were not affected by the biomass size. Wang et al. [100] torrefied sawdust using carrier gases containing 0, 3 and 6 vol% of O_2 at 250, 270 and 290 °C followed by pelletization. They found that the properties of oxidatively torrefied sawdust and its pellets, such as density, energy consumption for pelletization, HHV and energy yield, were close to those of non-oxidatively torrefied sawdust.

3.5.2. Wet torrefaction

Instead of biomass torrefied in the gas phase, wet torrefaction means that biomass is pretreated in the liquid or aqueous phase. Wet torrefaction is also called hydrothermal carbonization. The reactions of biomass in liquid water do not proceed significantly when the temperature is below 180 °C. Therefore, wet torrefaction is commonly carried out at temperatures of 180–260 °C [110]. This implies that biomass is immersed in solutions with gauge pressure up to 4.69 MPa. The reaction time of wet torrefaction is usually in the range of 5–240 min. The energy density of biomass is intensified with its heating value being increased by 3–47% [110]. Meanwhile, the biomass after hydrothermal carbonization treatment also becomes hydrophobic [111].

The study of Yan et al. [38] concerning the pretreatment of loblolly pine suggested that wet torrefaction (hot compressed water at 200–260 °C for 5 min) was more successful than dry torrefaction (N_2 at 250–300 °C) in energy densification under similar mass yield. Similar to dry torrefaction, the reaction temperature had a significant influence on the reaction mechanism and production distribution in wet torrefaction [112]. Because biomass is upgraded in liquid water, some acids or other materials can be added into liquid water to improve the performance of wet

torrefaction. Chen et al. [53] pretreated bagasse in dilute acid solutions with microwave-assisted heating and reported that the addition of sulfuric acid and increasing heating time were conducive to carbonizing bagasse. Lynam et al. [110] used acetic acid and/or lithium chloride solutions to pretreat loblolly pine at 230 °C for 5 min and found that the addition of acetic acid and/or lithium chloride also increased energy density of solid product. Alternatively, Chen et al. [53] found that wet torrefaction could be carried out at temperatures about 100 °C lower than that of dry torrefaction to achieve the same improvement in calorific value. Although the wet torrefaction treatment has to be taken place under high pressure, it seems to be also a promising method to upgrade biomass feedstock because of its low temperature operation.

3.5.3. Steam torrefaction

In addition to wet torrefaction, biomass can also be torrefied using saturated steam, so-called steam explosion treatment, or superheated steam. Steam explosion has been widely employed to pretreat biomass for the production of lignocellulosic bioethanol [7]. In recent studies [113–116], attention is also paid to the impact of steam explosion on the properties of residual solid biomass for manufacturing pellets. Steam explosion is usually carried out at temperatures 200–260 °C for 5–10 min followed by rapid decompression [113]. After undergoing steam explosion, low molecular weight volatiles are removed with the calorific value and carbon content of biomass being increased, whereas its bulk density, mean particle size and equilibrium moisture content decreased [116]. Similar to conventional dry torrefaction, an increase in steam temperature or explosion time intensifies the severity of torrefaction [115]. Compared to dry torrefaction, steam explosion is able to increase the calorific value, hydrophobicity and carbon content at much lower temperatures and shorter treatment time [116]. Moreover, the produced pellets from steam explosion treatment have higher mechanical strength and elasticity than untreated pellets [114,115].

4. Potential applications

4.1. Densification

Biomass densification (also called pelletization) is a process applying a mechanical force to compact biomass residues or wastes (sawdust, shaving, chip or slab) into uniformly sized solid particles such as pellets, briquettes and logs. The objectives of biomass densification are to increase the volumetric energy density from the initial 40–200 $kg\ m^{-3}$ to the final 600–1400 $kg\ m^{-3}$, to facilitate easy storage and handling, to reduce the transportation cost, and to lower the moisture content [117–122]. The quality of densified pellets strongly depends on the fiber sources, particle size, particle moisture content, particle temperature, biomass feed rate, die size and shape, compacting speed and die temperature [123]. The effort to reduce greenhouse gas emissions and the rising oil and natural gas prices drive the rapid growth of wood pellet industry in the world. Currently, wood pellets are considered as a major transportable renewable energy source.

The densification of torrefied biomass samples was more difficult under the same operating conditions as used for the densification of untreated samples [124,39,125,126,21]. Precondition of torrefied sawdust, high compression pressure and high die temperature are required to produce torrefied pellets of a quality similar to regular pellets. There has been no commercial torrefied pellets production process.

4.1.1. Density of torrefied pellets

The density of torrefied pellets can be improved by preconditioning the torrefied sawdust before compression. Phanphanich [124] reported that single torrefied pellet density could reach 1032 kg/m³ when the torrefied sample was preconditioned to 3.5–10.5 wt% moisture content. Similarly, Peng et al. [17] reported that torrefied samples preconditioned to around 10% moisture content could result high quality torrefied pellets. However, the single torrefied pellet density made from preconditioned torrefied samples was still lower than control pellets made from untreated sawdust samples [124,17]. Pyle [127] suggested that a die temperature of 93 °C could be used to make durable torrefied pellets without any binder, while Verhoeff et al. [126] reported that torrefied pellets with a density higher than control pellets could be obtained when a die temperature of 260 °C was used to compress torrefied sawdust prepared at 280 °C. A systematical investigation was conducted by Peng et al. [21,22] on the effects of preconditioning (conditioned to 0–15% water content), die temperature (from 70 to 280 °C) and compression pressure (from 125 to 280 MPa) on the density of torrefied pellets (see Fig. 11), who found that to make torrefied pellets of density similar to the control pellet the suitable die temperature ranges from 170 to 230 °C for unconditioned samples or about 110 °C for samples preconditioned to 10% moisture content. The torrefied pellet density decreased with increasing the weight loss [20,22], and the energy consumption for making pellets increased as the torrefaction temperature increased [21].

4.1.2. Hardness of torrefied pellets

Strong pellets, as characterized by a high mechanical strength, can reduce the breakage during handling, transportation, and storage. The mechanical durability for large quantity of briquettes and pellets can be determined in a tumbling device following the international round robin test procedure [128]. For single pellet or small samples of pellets, the pellet strength, as represented by its hardness, has been commonly determined by applying a force to deform or break the pellet located between a mobile probe and a fixed plate [129,20,17,21,22]. According to Peng et al. [22], the Meyer hardness (H_M) can be calculated by

$$H_M = \frac{F}{\pi \sqrt{Dh - h^2} \sqrt{\frac{D_p^2}{4} - \left[\frac{(D_p^2/2) + (DD_p/2) - Dh - D_p h + h^2}{D + D_p - 2h} \right]^2}}$$

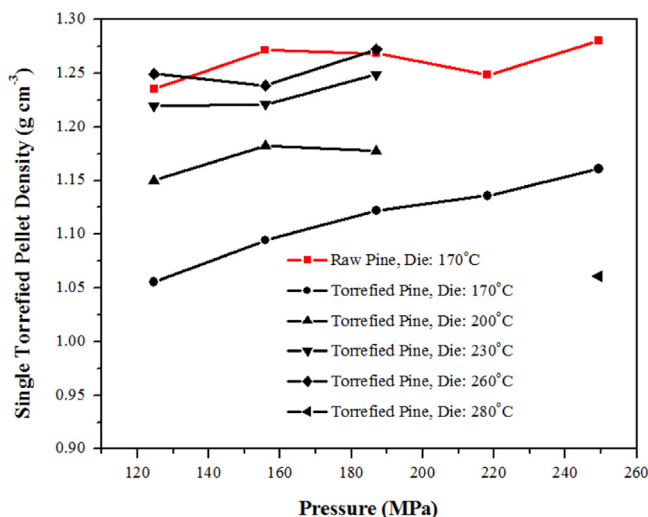


Fig. 11. Density of single torrefied pellet as a function of compression pressure and die temperature [21].

where F is the maximum force to break a pellet, D is the probe diameter, h is the indentation depth corresponding to the piston displacement before the pellet breakage, D_p is the pellet diameter.

Li et al. [20] reported that the Meyer hardness of torrefied pellets made at a die temperature of 170 °C was lower than control pellets. With preconditioned sample compressed at a die temperature of 110 °C, torrefied pellets also had a lower hardness than control pellets [22]. Verhoeff et al. [126] reported that torrefied pellets made at a die temperature of 225 °C was 29% stronger than control pellets, and torrefied pellets made at 260 °C die temperature was 103% stronger than control pellets. Peng et al. [21] also reported that the Meyer hardness of torrefied pellets is higher than the control pellets when the die temperature is higher than 240 °C. At 260 °C die temperature with 187 MPa compression pressure, the torrefied pellets are 1.24 times as strong as the control pellets (see Fig. 12). All those results suggest that a die temperature more than about 200 °C is needed to make strong torrefied pellets.

4.1.3. Moisture uptake of torrefied pellets

Pellets of a low hygroscopicity or high water-resistance can reduce the cost associated with pellets handling and storage, and prolong their shelf-life. The moisture uptake of torrefied pellets was examined in the humidity chamber at 30 °C and 90% relative humidity [20–22]. The saturated moisture uptake of torrefied pellets as obtained by leaving the pellets in the humidify chamber for more than 48 h was found to be much lower than regular control pellets. Verhoeff et al. [126] reported that for torrefied pellets prepared at 225 °C die temperature, the final moisture uptake was only 40% of the control pellets, and 10% for pellets made at 260 °C die temperature. The saturated moisture uptake of torrefied pellets mainly depended on the torrefaction condition. As shown in Fig. 13, the saturated moisture uptake of torrefied pellets was around 10% for torrefied samples with 34% weight loss, which is about 40% lower than the control pellets of 19%. The saturated moisture content of torrefied wood pellets decreased steadily with the increase in the mass loss or the degree of torrefaction [22].

4.1.4. Economics of torrefied pellets

Due to their high heating value, good water-resistivity and durability, torrefied wood pellets are considered as the 2nd generation of wood pellets, having a great potential to be used in thermal power plants and metallurgical processes to replace

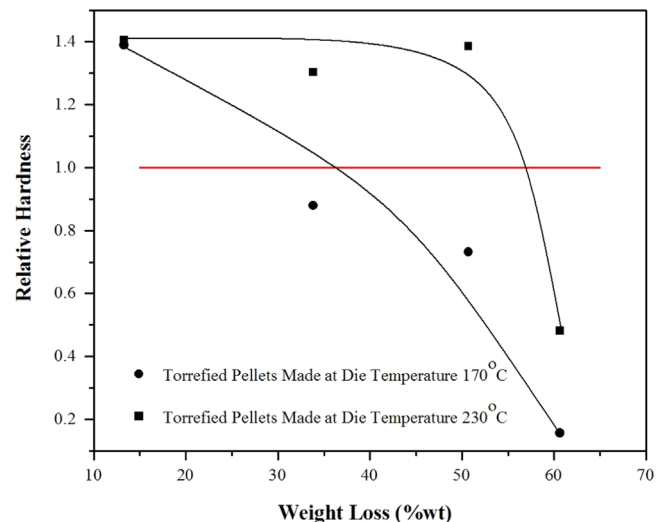


Fig. 12. Relative hardness of torrefied pellets over the regular pellets as a function of torrefaction weight loss [21].

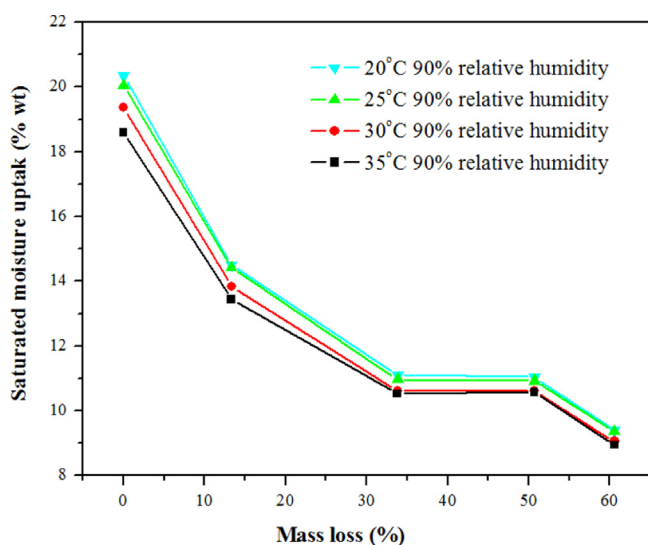


Fig. 13. Saturated moisture uptake of torrefied pellets as a function of torrefaction weight loss [22].

coal. Economically, it has been shown [130,131] that the overall cost, which including the production, transportation and logistics costs, for torrefied pellets can be cheaper than regular pellets, 4.7 Euro/GJ for torrefied pellets vs. 5.8 Euro/GJ for production in Europe [129] or \$7.6/GJ for torrefied pellets vs. \$8.6/GJ for regular pellets for Canadian pellets sold in European market [132]. This mainly results from the savings associated with the transportation and logistics of torrefied pellets due to their high energy density and hydrophobicity.

4.2. Gasification

In a gasification process, biomass is converted to synthesis gas or syngas (i.e., $H_2 + CO$) from fuels in an oxygen-deficient environment. On account of the improvement in biomass properties from torrefaction, torrefied biomass rather than raw biomass as a feedstock is expected to improve the gasification efficiency and lower the tar formation because of its high heating value and low volatiles content.

As Prins et al. [16] pointed out, the gasification temperature of raw wood was lower than that of torrefied wood at a fixed air-to-biomass feed ratio due to the high O/C ratio and high moisture content in the raw biomass. As a result, wood was generally over-oxidized in a gasifier, which led to a higher thermodynamic loss. Torrefaction could decrease the moisture content and the O/C ratio in biomass, thereby reducing the thermodynamic loss in gasification. Deng et al. [44] proposed a conceptual system for combined coal gasification and biomass torrefaction. Couhert et al. [133] investigated the impact of torrefaction on the production of syngas from wood gasification in an entrained-flow reactor, and found that less chars were generated from torrefied wood as the feedstock, and the quantity of produced syngas increased with increasing torrefaction severity. Strega et al. [134] used blends of subbituminous coal, torrefied biomass, and untreated biomass to study their gasification performance in a bench-scale oxygen-blown fluid-bed gasifier that was coupled to a modular fixed-bed Fischer–Tropsch reactor. Their results indicated that the bed temperature diverged rapidly and material agglomeration occurred in the bed when a blend of coal and torrefied biomass was replaced by a blend of coal and raw biomass. Therefore, using torrefied biomass as the feedstock for gasification was effective to reduce the tendency for the formation of agglomerates. Torrefaction has also been applied in a two-stage gasification process to

lower tar content in the gasification syngas for the production of high-quality syngas for biofuels/chemicals. The two-stage gasifier consists of a torrefaction reactor followed by a high temperature gasification reactor to convert the pyrolysis vapors by reforming and cracking catalyzed by char. At the same time, the char and the soot (carbon black from volatiles) are gasified in the gasification reactor to obtain a synthesis gas with a very low content of tar [135,136].

To evaluate the potential use of torrefied biomass for gasification, Chen et al. [137] experimentally studied sawdust gasification in an entrained-flow gasifier. They found that syngas quality and cold gas efficiency from the gasification of torrefied sawdust were better than those from raw sawdust, and the gasification of sawdust torrefied at 250 °C gave the best results. Chen et al. [138] compared the gasification of raw bamboo and torrefied bamboo (at 280 °C for 1 h) to that of a high-volatile bituminous coal in an entrained-flow gasifier using O_2 as the gasification agent. They found that the cold gasification efficiency of raw bamboo was low; the gasification performance of the torrefied bamboo fuel was enhanced significantly and close to the coal gasification under the same operating conditions. Under optimum conditions of the equivalence ratio, the cold gas efficiency of torrefied bamboo was improved by 88% over the raw bamboo as the feedstock. The thermodynamic analysis of Kuo et al. [139] also indicated that biomass undergoing torrefaction was conducive to increasing syngas yield from gasification. In general, the higher the torrefaction temperature, the higher the syngas yield. The numerical analysis of Chen et al. [138] using a Taguchi approach revealed that torrefaction was an important step in determining the performance of co-gasification of biomass and coal. The evidences from the above-mentioned studies suggest that torrefaction is a potential method to achieve more efficient gasification of biomass.

4.3. Ironmaking

Blast furnaces are a key facility employed in ironmaking for producing hot metal [140–142]. Alternating layers of coke and ore burden are charged from the top of the furnace, whereas blast air and pulverized coal are injected from the bottom through blowpipes, injection lances and tuyeres [143]. In modern blast furnaces the consumption amounts of coke and coal are around 300–350 and 150–200 kg per tonne hot metal ($kg\ tHM^{-1}$), respectively [144]. To reduce the utilization of fossil fuel, biomass can potentially replace coal in metallurgical coke production, iron ore agglomeration and pulverized coal in tuyere injection [144,145]. Charcoal has been considered as a possible substitute to be partially blended with metallurgical coke as the reducing agent [146]. Compared to charcoal, the carbonization of biomass from torrefaction is less violent. Therefore, torrefied biomass may be more suitable to be used for pulverized coal injection in blast furnaces.

By virtue of a considerable amount of coal consumed in blast furnaces through pulverized coal injection to provide heat for reducing iron ore [147], carbon dioxide emissions from the furnaces is a noticeable issue in ironmaking processes. As a matter of fact, the steel industry accounts for 5–7% of total anthropogenic CO_2 emissions in which around 70% of CO_2 emissions come from iron production in blast furnaces [148]. This implies, in turn, that CO_2 liberated from blast furnaces account for approximately 3.5–5% of total anthropogenic CO_2 emissions. Therefore, if CO_2 emissions from blast furnaces can be substantially reduced, it will give a significant contribution to mitigating atmospheric greenhouse effects. From the alternative fuel point of view, if pulverized coal can be replaced by biomass in part, it will be an effective countermeasure to lessen CO_2 emissions from blast furnaces.

When coal particles are injected, they proceed from the blowpipe, tuyere, and then to the raceway. In this process the fuel experiences rapid heating (the heating rate is around 10^5 K s^{-1}), devolatilization, gas phase combustion and char combustion and gasification [145]. Drop tube furnaces (DTFs) are the most commonly used devices [149,150] to simulate coal particle reactions when the particles are injected into the blast furnace. This arises from the fact that the furnaces can be utilized to evaluate the combustion performance of pulverized coal in an environment with high heating rate. In the study of Chen et al. [43], the torrefaction and burning characteristics of bamboo, oil palm, rice husk, bagasse and Madagascar almond were studied and compared with a high-volatile bituminous coal using a DTF and the ash tracer method to evaluate the potential of biomass use in blast furnaces. Their results suggested that torrefaction at 300°C was a feasible operating condition to transform biomass into a solid fuel resembling a high-volatile bituminous coal used for blast furnaces.

5. Summary and future work

Torrefaction as a biomass pretreatment technique has been extensively studied in recent years to explore its potential applications for improving the gasification performance and the production of 2nd generation wood pellets of comparable quality to replace thermal coal and metallurgical coal in power plants and blast furnaces. Torrefaction kinetics has been systematically investigated using variety biomass species and their major components, lignin, cellulose and hemicelluloses, under both inert (N_2) and oxidative (O_2 , H_2O) environments. The higher heating value, hardness and saturated moisture content of torrefied pellets were found to be a strong function of weight loss, which represents the degree of torrefaction. Torrefaction also improved the biomass grindability substantially. The gasification of torrefied biomass was able to improve the gasification thermal efficiency and reduce tar formation because of the removal of oxygenated volatile compounds. It is more difficult to compress torrefied sawdust into pellets, which requires higher die temperature and mechanical energy to make torrefied pellets of similar density and hardness as regular pellets. However, because of the potential savings from pellets transport, handling and storage logistics, the overall cost for torrefied pellets can be comparable to, if not lower than, regular wood pellets in European market for pellets made in both European and North America.

In view of the great potential markets of torrefied pellets for replacing thermal and metallurgical coal in power and metal industries, future work should be focused on the develop integrated torrefaction and gasification processes for high-quality syngas production, and integrated torrefaction and densification processes for the production of torrefied pellets. Up to now, most studies have been conducted in laboratory scale reactors, pilot and demonstration scale tests should be carried out to investigate the scaleup effects and examine the energy integration in a commercial system.

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